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DIFFUSION KINETICS OF HETEROGENEOUS CHEMICAL PROCESSES:
I. REACTION WHICH TAKES PLACE AT THE SOLID-LIQUID INTERFACE

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General Concepts

The total speed of any heterogeneous chemical conversion consists of the
speed with which the reagents are transported to the place of reaction and the
speed of the chemical reaction as such. The speed of the chemical conversion
is of particular interest to the chemist -- for that reason the diffusion ki-
netics of heterogeneous chemical reactions in solution have been neglected
hitherto, and no well developed quantitative theory exists. An attempt is be-
ing made to fill this gap. This paper deals with reactions at the solid-liquid
interphase for laminar flow; the second paper will develop the theory for tur-
bulent flow; the third paper will deal with reactions at the liquid-liquid
rather than solid-liquid interphase; and the fourth will analyze cases of com-
posite kinetics.

In practice, a liquid which transports matter usually flows so fast that
the flow takes place at large Reynolds' numbers, for a hydrodynamic boundary
layer develops on the surface of the solid and sometimes essentially turbulent
conditions are established.

Hitherto Nernst's theory of the motionless diffusion layer, with a con-
stant concentration in the body of liquid due to stirring, has been used uni-
versally almost without change. The diffusion current (j) in accordance with
that theory can be expressed mathematically as follows:

$$j = D \frac{C_0 - C_1}{\delta},$$

C_1 = concentration at the place of reaction, i.e., on the surface of the
solid.

C_0 = concentration at the outer boundary of the diffusion layer, which
is equal to the average concentration of the entire solution.

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δ - width of the diffusion layer.

The values of δ determined by experiment from observed values of j are found to be dependent upon the flow velocity u of the liquid, its viscosity η, and the diffusion coefficient D. Absolute values of δ of the order $10^{-2} - 10^{-4}$ centimeters were found by using the expression for Nernst's diffusion layer, while the actual layer thickness found from hydrodynamic experiments is much smaller. The divergence between Nernst's theory and experimental results had been noted long ago, but the attempts to develop a new theory (Eucken, Frank-Kamenetskiy) did not go far enough. On the other hand, a theory developed by the author in connection with the treatment of concentration polarization in electrolysis (cf. Zhur. Fiz. Khim, Vol 13, p 355, 1944) was found to be fully applicable in the generalized case not involving ions.

The complicated equations of Navier-Stokes, which deal with the stationary flow of viscous liquids and relate the velocity components V_i of the liquid and the pressure (p) in it to external forces acting upon the body of the liquid, can be considerably simplified to cover the conditions involved in this case. At high Reynolds' numbers, the flow can be regarded as consisting of two regions -- the region of nonviscous flow at a distance from the solid surface and the region of viscous flow in direct proximity to that surface (Prandtl boundary layer theory).

Assuming that the boundary layer is very thin (a condition corresponding to the actual state of affairs in this case), it is obvious that the speed will change rapidly in a direction perpendicular to the surface of the solid, but not along this surface. Directing the y axis perpendicularly to the wall, assuming that the flow takes place along the x axis, and making a few further simplifications, the equations of Prandtl are obtained from the Navier-Stokes equations. Applying Prandtl's equations to flat solid bodies or those having a small curvature, the following working relationships are obtained for the effective thickness of the boundary layer (δ_0)

$$\delta_0 = 4.90 \sqrt{\frac{\nu x}{U}} \tag{1}$$

(u = rate of flow outside of the boundary layer) and for the components of velocity.

$$\mathcal{V}_x = \frac{Uy}{\delta_0} + \cdots, \tag{2}$$

$$\mathcal{V}_y = \frac{\nu y^2}{\delta_0^3}$$

Diffusion Boundary Layer

In formulating the basic equations for the transport of a substance to the reaction surface in a moving liquid, the so-called Pekle's number (indicated as Pe) can be introduced to advantage. Pekle's number is similar to Reynolds' number, except that it measures diffusion rather than the flow of liquid. Comparing Pekle's number with Reynolds number, we obtain Prandtl's number (9).

$$\text{(3)} \quad P_e = \frac{\left| \mathcal{V}_i \left(\frac{\partial C}{\partial x_i} \right) \right|}{\left| D \frac{\partial^2 C}{\partial x_i^2} \right|} \approx \frac{Ul}{D} \qquad P_r = \frac{\nu}{D} \tag{4}$$

In liquids Prandtl's number is always large in comparison with unity. In gases, on the other hand (flow of fluid in this case), Prandtl's number is of the order of unity.

Because of the small value of the diffusion coefficient, Pekle's number attains large values even for the lowest velocities, even when the corresponding Reynolds' number is still small in comparison with unity. Therefore, molecular diffusion in liquids may practically always be disregarded in comparison with the convective transport of a substance. For large Pekle's numbers,

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the same reasoning may be applied to convective diffusion as was applied previously to the flow of a liquid around a body for large Reynolds' numbers.

The concentration of the substance in the main body of the solution is constant. However, this condition cannot obtain at the reaction surface. A thin layer in which a rapid change of concentration takes place must exist close to the reaction surface.

For large Pekle's numbers, the entire liquid may be broken down into two regions, as was done for large Reynolds' numbers; i.e., the region of constant concentration remote from the reaction surface and the region of rapid change in concentration bordering directly on this surface. The latter region, a very thin layer of liquid, is similar to the Prandtl boundary layer; the viscosity of the liquid, which is basically unimportant in the flow volume, plays a substantial role in the Prandtl boundary layer, while molecular diffusion appears in the liquid layer adjoining the reaction surface. This layer can be described as the diffusion boundary layer.

The concept of diffusion boundary layer is obviously a generalization and refinement of Nernst's concept of a layer. The real difference in the two concepts is the fact that a liquid's velocity of flow in a diffusion boundary layer can by no means be assumed to equal zero. On the contrary, the diffusion and convection flows of the substance here have the same order of values. The diffusion boundary layer is analogous to the heat boundary layer in the theory of heat transmission in liquids. There is, however, a real quantitative difference between them: the diffusion layer is several times thinner than the heat layer and therefore its other properties, for example, the spatial distribution of the substance, are different from the analogous properties of the heat boundary layer.

In the diffusion process, the role of kinematic viscosity is usurpedly by the coefficient of diffusion D which is numerically almost a thousand times smaller. Therefore, the diffusion boundary layer also must be considerably thinner than the Prandtl boundary layer.

The thickness of the diffusion layer is found to be

$$\delta \approx \left(\frac{D}{\nu}\right)^{1/3} \delta_0 = (Pr)^{-1/3} \delta_0.$$

Thus, for Pr approximately 10^3, the thickness of the diffusion boundary layer is approximately one-tenth the thickness of the Prandtl boundary layer. Therefore, the tangential component of the liquid's velocity of motion at the periphery of the diffusion boundary layer is only 10 percent of the velocity at a point remote from the solid surface. The following relationship can be derived:

$$\delta \approx D^{1/3} \nu^{1/6} \sqrt{\frac{x}{U_0}}. \tag{5}$$

This shows that the thickness of the diffusion boundary layer is inversely proportional to the square root of the velocity U_0 of the impinging flow and increases in proportion to the square root of the distance x from the advance point of the liquid flow to the body, the thickness is also dependent upon the liquid's viscosity and the coefficient of diffusion of the particles (see below).

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Calculations show that, in the diffusion boundary layer, the concentration of the solution increases rapidly and that the increase may be considered linear in the first approximation.

Therefore, the expression for diffusion current may be represented approximately in the form $j_{dif} = DC_0/\overline{D}$, i.e., in the same form as in Nernst's theory.

Now, however, $\overline{D}$ is a completely determined function of the liquid's properties and velocity.

The concentration distribution and the current magnitude may be found more accurately from a precise solution of the equation of convective diffusion. Several solutions of this equation for special applications are given below.

Solutions of Equations of Diffusion Kinetics

1. Convective Diffusion With Reference to a Rotating Disk

Problems in this connection are frequently encountered in electrochemistry. For the density of a diffusion current (j) at the surface of a disk it could be shown that

$$j = D \left(\frac{\partial C}{\partial y}\right)_{y=0} = 0.79 \left(\frac{\nu}{D}\right)^{1/3} \sqrt{\frac{\omega}{\nu}}, \qquad (6)$$

where ω = angular velocity of the disk.

2. Convective Diffusion for Streamlike Flow Passing a Plate

The full diffusion current (I_{lim}) on one side of the plate was found to be

$$I_{lim} = \frac{1}{2} \frac{C_f U_0 C_0 S}{Pr^{2/3}}. \qquad (7)$$

where C_f (the so-called drag coefficient) represents a ratio of the frictional force tangential to the plate to the dynamic head and can be expressed as follows

$$C_f = \frac{1.33}{\sqrt{\frac{xh}{\nu}}} = \frac{1.33}{\sqrt{Re}}.$$

3. Natural Convection at a Vertical Plate

In the preceding examples cases of forced convection were considered. At high Prandtl numbers, the following expressions apply for the density of the diffusion current at the plate (j), the full current (I), and the thickness of the diffusion current (δ')

$$j = 0.54 \, (Pr)^{1/4} \left[\frac{g \left(\frac{\partial \rho}{\partial c}\right)_{c=c_0} C_0}{4 \rho(C_0) \nu^2} \right]^{1/4} \frac{1}{x^{1/4}}$$

$$I = \int j \, ds = 0.72 \, (Pr)^{1/4} \left[g \left(\frac{\partial \rho}{\partial c}\right)_{c=c_0} \frac{C_0}{4 \rho(c) \nu^2} \right]^{1/4} b l^{3/4},$$

$$\delta' = \frac{x^{1/4}}{\left[\frac{Pr \, C_0 \left(\frac{\partial \rho}{\partial c}\right)}{4 \rho(C_0) \nu^2} \right]^{1/4}}.$$

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Thus, the thickness of the boundary layer slowly increases with the distance from the lower edge of the plate and is only slightly dependent upon the concentration of the solution.

4. The Problem of Internal Flow, Particularly in a Pipe

It is known that the parabolic profile of velocities, which is typical of the Poiseille flow in pipes, is established only in the so-called exit section of the pipe. At the entrance of the pipe a boundary layer is formed, the thickness of which grows gradually in the entrance section until the whole cross section of the pipe is filled by the layer, and further flow takes place according to Poiseille. The length of the entrance section is by no means small -- to give an example, it has the dimensions of 50 diameters at Re $\curvearrowright$ 2500. The same conditions obtain in regard to diffusion, except that the entrance section is much longer and may extend over the whole length of the pipe. For the region of Poiseille flow it can be shown that

$$ J = D \frac{\partial C}{\partial x} = \frac{3D}{x^{\frac{2}{3}}} \left(\frac{2 U_m}{3 RD} \right)^{\frac{1}{3}} \frac{C e^x}{\Gamma(\frac{1}{3})} $$

and

$$ \delta \approx \sqrt{\frac{RDx}{U_m}} $$

*/Exponent of X is unclear in the original; 4/3 appears to be the logical value./

The diffusion boundary layer fills the whole cross section of the pipe at

$$ x \approx \frac{U_m R}{D} R \approx Re \cdot Pr \cdot R. $$

As Pr $\curvearrowright 10^3$, the length of the entrance section becomes so long that it practically always extends over the whole length of the pipe.

Agreement With Experimental Data

In prior work done by the author, good agreement was obtained in experiments of an electrochemical nature. Because of the complex hydrodynamic condition encountered there, this agreement was qualitative rather than quanitative. In particular, the reason for the divergence of results obtained by various authors on the problem of dependence of diffusion current upon velocity was brought to light. Various authors pointed out the "potential" (exponential) nature of this dependence, but they differed on the value of the exponent, the indices ranging from 0.5 to 1; this circumstance was due to the different degrees of turbulence in the various experiments. A comparison was also made with experimental data on the dependence of current upon coefficients of diffusion and viscosity, good agreement being found in this case. Recently, Siver conducted special measurements to experimentally verify our formulas for flow around a rotating disk. These carefully conducted measurements showed that the theory for the disk is in good quanitative agreement with experiment (cf. Yu. Siver and B. Kabanov, Zhur Fiz Khim, Vol 22, p 53, 1948).

Nonetheless, a considerable part of the relations obtained are in need of further experimental verification, since the necessary experimental data are not to be found in print. This relates particularly to diffusion currents in the region of turbulent transport of substance in the boundary layer and at the interphase liquid-gas.

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